Diversification of Hydrothermal Reaction Products Induced by Temperature, Syntheses, Structures, and Properties of Four La(III)-Cu(II) Metal Frameworks Constructed from Rod-Shaped Molecular Building Blocks

Junwei Ye*^{, a}, Jingying Zhang^b, Ling Ye^b, Dong Xie^a, Tao Xu^a, Gang Li, Guiling Ning^{*, a}

^a State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, P. R. China

^b State key laboratory of supramolecular structure and materials, Jilin University, College of Chemistry, Jilin University, Changchun 130012, P. R. China

*To whom correspondence should be addressed. Fax: +86-411-88993609, E-mail: junweiye@dlut.edu.cn (J. Ye); E-mail: ninggl@dlut.edu.cn (G. Ning).



Scheme S1 Schemetic representation of the coordination modes of NIPH ligands in compounds 1-4. Mode I and II for 1, Mode III and IV for 2, Mode II and V for 3, Mode IV, VI and VII for 4.



Fig. S1 Experimental and simulated powder X-ray diffraction patterns of 1 (a), 2 (b), 3 (c) and 4 (d).



Fig. S2 Perspective view of the hydrogen-bond interactions and three-dimensional network in **1**.



Fig. S3 Perspective view of the hydrogen-bond interactions and three-dimensional network in **2**.



Fig. S4 Perspective view of the hydrogen-bond interactions and three-dimensional network in **3**.



Fig. S5 Perspective view of the hydrogen-bond interactions and three-dimensional network in **4**.



Fig. S6 Thermogravimetric curve for (a) 1, (b) 2, (c) 3, (d) 4.



Fig. S7 Temperature variation of the magnetic susceptibility χ_m and $\chi_m T$ for 4.

D-H…A	d(D-H)	d(H···A)	d(D····A)	<(DHA)
1	· ·	· ·	· · ·	· ·
O(15)-H(15A)···O(18)	0.82	2.03	2.847(6)	172.0
$O(17)-H(17B)-O(10)^{\#1}$	0.889(17)	2.06(3)	2.833(4)	144(4)
$O(14)-H(14A)\cdots O(3)^{\#2}$	0.82	1.87	2.684(4)	174.8
$O(14)-H(14B)\cdots O(4)^{\#3}$	0.902(18)	2.12(3)	2.814(5)	133(3)
$O(15)-H(15B)\cdots O(5)^{\#3}$	0.895(18)	2.42(3)	3.033(6)	126(3)
O(17)-H(17A)···O(4) ^{#4}	0.82	2.05	2.761(4)	145.3
O(16)-H(16A)····O(18) ^{#5}	0.82	2.15	2.935(6)	159.4
O(18)-H(18B)····O(6) ^{#6}	0.901(17)	2.38(3)	3.111(6)	139(4)
$O(17)-H(17B)\cdots O(3)^{\#7}$	0.889(17)	2.53(4)	3.190(5)	131(3)
$O(16)-H(16B)-O(12)^{\#8}$	0.885(18)	2.07(2)	2.832(6)	144(3)
2				
O(13)-H(13B)····O(9) ^{#1}	0.663(13)	2.513(13)	2.8565(16)	114.9(13)
$O(14)-H(14A)\cdots O(7)^{\#2}$	0.773(14)	2.186(12)	2.7841(14)	134.7(10)
$O(14)-H(14B)\cdots O(10)^{\#3}$	0.852(11)	1.978(11)	2.8246(17)	172.1(13)
$O(15)-H(15A)\cdots O(5)^{#4}$	0.657(12)	2.325(12)	2.9801(16)	174.3(15)
$O(13)-H(13A)\cdots O(11)^{\#5}$	0.735(10)	2.232(11)	2.9638(18)	173.3(14)
O(15)-H(15B)····O(6) ^{#6}	0.765(11)	2.176(12)	2.9366(16)	172.5(14)
3				
$O(13)-H(13A)-O(11)^{\#1}$	0.82	2.15	2.945(14)	162.1
4				
O(20)-H(20B)···O(13)	0.789(18)	2.24(4)	2.951(7)	151(7)
$O(20)-H(20A)\cdots O(10)^{\#1}$	0.81(8)	2.56(8)	2.986(7)	115(6)
$O(21)-H(21B)\cdots O(4)^{\#3}$	0.79(8)	2.20(8)	2.834(7)	137(7)
$O(21)-H(21A)\cdots O(22)^{\#4}$	0.87(8)	1.98(8)	2.813(9)	160(7)
$C(12)-H(12)-O(2)^{\#4}$	0.76(8)	2.70(8)	3.443(7)	169(7)
$O(20)-H(20A)\cdots O(5)^{\#5}$	0.81(8)	2.25(8)	2.898(7)	137(7)
$O(22)-H(22A)\cdots O(18)^{\#6}$	0.89(8)	2.17(8)	2.976(11)	151(7)
$O(15)-H(15A)\cdots O(3)_{\mu}^{\#/2}$	0.89(8)	1.71(8)	2.574(6)	165(7)
$C(10)-H(10)\cdots O(21)^{\#8}$	0.94(8)	2.41(8)	3.303(7)	160(6)
$O(19)-H(19B)\cdots O(21)^{\#8}$	0.79(8)	2.11(8)	2.841(8)	155(8)
$O(22)-H(22B)\cdots N(2)^{\#9}$	1.05(8)	2.61(8)	3.632(8)	164(6)
$O(22)-H(22B)\cdots O(11)^{\#9}$	1.05(8)	1.78(8)	2.825(8)	172(6)
$O(19)-H(19A)\cdots O(21)^{\#10}$	0.68(8)	2.07(8)	2.737(7)	166(9)

Table S1 Hydrogen bonds for **1-4** [Å and °]

Symmetry transformations used to generate equivalent atoms: For 1: #1 x,y-1,z; #2 -x,-y+1,-z+1; #3 x,y+1,z; #4 x+1,y+1,z; #5 x+1,y,z; #6 -x+1,-y+1,-z+2; #7 -x+1,-y+1,-z+1; #8 -x+2,-y+2,-z+2. For 2: #1 -x+1,-y+2,-z+1; #2 -x+1,-y+1,-z+2; #3 x+1,y-1,z; #4 x-1,y+1,z; #5 -x,-y+2,-z+2; #6 -x+3,-y+1,-z+1. For 3: #1 x, y+1, z-1. For 4: #1 x+1,y,z; #2 x,y+1,z; #3 -x+1,-y+2,-z+1; #4 x-1,y,z; #5 x,y-1,z; #6 -x+1,-y+1,-z+1; #7 -x+1,-y+1,-z; #8 -x,-y+1,-z+1; #9x+1,y-1,z; #10 x,y,z-1.